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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re. Application of:

Bing Zhou et al

Art Unit: 1754

Serial No. 10/038120

Examiner: C. Nguyen

Filed: November 9, 2001

Date: April 4, 2002

For: Catalyst and Process for
Oxidation and Removal of Nitrogen Oxides
(NO_x) from Combustion Gases



PRELIMINARY AMENDMENT UNDER 37 CFR 1.115

Commissioner of Patents and Trademarks

Washington, DC 20231

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Prior to examination of the above-identified continuation-in-part patent-application, applicants respectfully request that the arguments presented below should be considered by the Examiner.

Following a personal interview by applicant Bing Zhou and the undersigned agent with Examiner C. Nguyen on September 19, 2001 for discussing the claims, prior art, and technical issues involved in the parent patent application Serial No. 09/225,082, the Examiner issued an Advisory Action dated October 15, 2001, stating that the Amendment Under 37 CFR 1.116 filed September 24, 2001 failed to place the application in condition for allowance. The reasons given were that the amendment raised new issues regarding the claim amendment language "so as to form a metal oxide complex" which were not adequately supported in the specification. Consequently, the above-identified C-1-P application was filed including some additional subject matter and revised claims which define the invention more accurately. The information previously submitted by a declaration under 37 CFR 1.132 has now been included in this C-1-P patent application.

For this invention, applicant has developed and disclosed a new and unique bi-functional catalyst material and method steps for making it, which catalyst is very effective for catalytic oxidation and removal of nitrogen oxides (NO_x) from various combustion gases. Because of its unique metal oxide complex structure and the method steps required for making it, this bi-functional catalyst provides both an adsorption metal oxide(s) and an oxidation metal oxide(s) which are chemically bonded intimately together by use of a binding agent acid so as to form a metal oxide complex having a crystalline form or structure. Such unique catalyst structure advantageously provides for effective simultaneous catalytic adsorption and oxidation of the nitrogen oxides (NO_x) contained in combustion gases derived from burning of various hydrocarbon fuels.

The claimed bi-functional catalyst structure and method steps used for making it are significantly different from the catalyst material and method steps as disclosed by the patents U.S. 5,756,057 (Tsuchitani) and U.S. 5,759,947 (Zhou) cited against claims of the parent application Serial No. 09/225,082, in that the adsorption metal oxide component and the oxidation metal oxide component are chemically bonded together so that their sites are very closely adjacent to each other in an orderly pattern. Such close intimate relationship is provided by use of a binding agent acid added to the metal ion solution in suitable molar ratio during making of the catalyst, so that during a subsequent calcining step the adsorption metal oxide and the oxidation metal oxide are chemically bonded together so as to form a metal oxide complex having a crystalline structure. The significant structural differences between catalyst samples made according to teachings of the two cited references and catalyst samples made according to the teachings of applicants' claimed invention were verified by X-ray diffraction (XRD) analysis. In the present C-I-P application, claims 1-7 are directed to the bi-functional catalyst material, and claims 8-16 are directed a method for making the bi-functional catalyst. Claims 17-29 are directed to a process for catalytic oxidation and removal of nitrogen oxides (NO_x) contained in fuel combustion gases, which process utilizes the bi-functional catalyst as defined by Claim 1.

Claims in the parent application were previously rejected under 35 U.S.C. 103(a) as being obvious in view of Tsuchitani et al (U.S. Pat.5,756,057). The Examiner contended that Tsuchitani et al disclose a catalyst which comprises platinum and/or palladium for oxidizing NO_x

(see col 8, ln 24-26), the alkali metals such as lithium, sodium, potassium, rubidium, and cesium or compounds thereof, and/or alkaline earth metals such as magnesium, calcium, strontium, and barium or compounds thereof for adsorbing NO_x (see col 8, ln 46-50), and further discloses that the catalyst comprises at least one metal selected from the group consisting of manganese, copper, cobalt, etc. or compounds thereof as another catalytically active component for promoting the oxidation and adsorption of NO_x (see col. 8, ln 68-col. 9, ln 9), and that lanthanum oxide is also suitable (see col. 11, ln 27). The support material is an inorganic metal oxide such as alumina, having surface area of 10 to 400 m²/g, (see col. 9, ln 18-30). The instantly claimed molar ratios of the adsorption and oxidation metal oxides are disclosed at col. 2, ln 45-65. The Examiner also contended that while this Tsuchitani et al patent does not indicate whether the adsorption and oxidation metals in the catalyst are combined intimately together, it is obvious that these catalyst metals are being mixed together because he teaches the same catalyst. The Examiner did not see a patentable distinction between the claimed bi-functional catalyst and the reference catalyst of Tsuchitani et al, as was explained in the final Office Action at page 5-6. Applicants again respectfully disagree with this rejection, because the cited reference does not teach or suggest the catalyst structure and method for making it per applicants' invention as now being claimed.

Tsuchitani et al, (US patent 5,756,057.) disclosed using noble metals from the group consisting of Mn, Cu, Co, Mo, W, and V as the oxidizing component and alkali metal as adsorbing component for NO_x removal from exhaust gases. But these two types of metal oxides are not chemically bonded together in close intimate contact utilizing a binding agent acid in such manner so as to form a metal oxide complex having a crystalline form or structure between the adsorption metal oxide component and the oxidation metal oxide component within close molecular distances, as now required for applicant's claimed invention. Tsuchitani et al apparently used the traditional wet-impregnation method for simply mixing the metal oxides together to prepare their catalyst. Also, their overall process concept was to convert NO first to NO₂, and then reduce NO₂ to N₂ by utilizing a reducing agent such as propylene. Their catalyst adsorbing sites were used to adsorb the oxidized NO₂ for the reduction to N₂ by propylene on surface. Without this adsorbing site, NO₂ will be released to gas phase, and it will not be possible to further react with propylene for reduction to NO₂. But in important contrast, applicants'

catalyst does not require or utilize such a reducing agent for removal of nitrogen oxides (NO_x) from combustion gases.

It is apparent that this approach taken by Tsuchitani et al for making a catalyst is substantially different from applicants' disclosed concept for a bi-functional catalyst structure and method for making same. For applicants' catalyst and method, it is emphasized that the adsorption metal oxide component and the oxidation metal oxide component are chemically bonded together in a metal oxide complex structure that is significantly different from that disclosed by the cited Tsuchitani et al patent. These structural differences were established by performing X-ray diffraction (XRD) measurements on samples of applicants' catalyst and those prepared according to teaching of Tsuchitani et al. These structural differences were verified by Professor W.H. McCarroll of Rider University, who performed the XRD measurements and provided a detailed report letter. Due to the innovative method steps that applicants used in making the bi-functional catalyst by utilizing a binding agent acid or its salt to bring the two types of metal oxide components and sites closely together; these metal oxides are placed closely adjacent to each other within molecular nanometer distance so that during subsequent calcining step form a metal oxide complex having a crystalline structure. The adsorbing sites adsorbs NO, and the closely adjacent oxidizing sites simultaneously converts and removes the NO from the combustion gas. This unique catalyst structure results in more effective oxidation of NO at temperatures much lower than achieved for other published data, and with significantly higher NO removal efficiency. Applicants' best results showed that at 427°F (220°C), 96% NO was oxidized and even at 326°F (163°C), 88% NO was converted (see application, Tables 1 and 2). If the adsorption and oxidation types of metal oxide sites were not chemically bonded closely adjacent within molecular nanometer distances in a metal oxide complex structure, it would not be possible to achieve such high NO_x removal efficiency at such low reaction temperatures.

Further regarding Tsuchitani et al (US patent 5,756,057), it is noted that when the catalysts were used to oxidize NO without utilizing a reducing agent such as propylene, the removal efficiency was very low. In all cases, even when the reaction was carried out at 400°C, the removal was always at or below about 20% (Table 1, control 2). High percentage removal of NO can be achieved only when a complicated procedure is followed, that is starting with 2% oxygen, adjusting the oxygen concentration to 0.4% when introducing reducing agent propylene

to the system, and then adjusting the oxygen concentration back to 2% when propylene is absent. With such complicated operation, the NO removal could reach 96% in some cases. However, the procedure is so complicated that it is not applicable to the large scale NO_x treatment, since the exhaust gas from power plant and other fossil fuels burning always contains a significant amount of oxygen (5-10%), and is economically impossible to reduce it to 0.4%. Obviously, the catalysts of Tsuchitani et al are significantly structurally different and much less effective than that invented and claimed by applicants. For these reasons, the bi-functional catalyst as now defined by catalyst composition claims 1-7 are considered patentable and should be allowed.

The method claims for making the catalyst were previously rejected under 35 U.S.C. 103(a) as being unpatentable over Tsuchitani et al. (U.S. Pat, 5,756,057) taken together with Zhou (U.S. 5,759,947). The Examiner contended that Tsuchitani et al disclose a process of making a catalyst comprising impregnating a support material with a mixed solution of catalytically active components which include both the suitable adsorption metal components and oxidation metal components (see col. 10, ln 40-46), and also discloses drying and calcining the catalyst at a temperature of 500°C for 2 hours (see Examples). Specifically regarding applicant's method claims, the Examiner contended that the difference between Tsuchitani et al and these claims is that Tsuchitani does not specifically disclose a binding acid or citric acid, but that it would have been obvious to one of ordinary skill in the art to have utilized these binding acids in the method of Tsuchitani, because they have been used in the method of Zhou (see Zhou col. 3, line 25 and Example1, line 26) in order to make a bi-functional catalyst having good properties, such as completely oxidizing various organic compounds and decomposing nitrogen oxides (see Zhou col. 1, lines 45-50), such as those catalysts which applicants desired. Also, while Tsuchitani et al do not specifically disclose cooling of the catalyst material, it would have been obvious at the time the invention was made to have cooled the catalyst material of Tsuchitani et al, because it is necessary to cool the catalyst to facilitate subsequent handling. Applicants respectfully disagree with this rejection for the reasons provided below.

H. Zhou (US 5,759,947) discloses a bi-functional catalyst containing multi-metal oxides and using a coordination agent such as citric acid to make the active metal compounds distribute on the support firmly and uniformly. The bi-functional catalyst of Zhou is specifically described by the inventor as " not only an oxidative catalyst but also a reductive one" (column 1, line 59).

Thus the metals used in this patent are those that have only oxidative and reductive properties, as no adsorption metals were considered. The citric acid used here was only to help distribution of the metals on the support and the calcining temperature did not exceed 300°C.

But in significant contrast to Zhou, for applicants' invention the specific method steps used to chemically bond together the adsorption metal oxide component and the oxidative metal oxide component at temperature of 500-800 °C are significantly different from those disclosed by Zhou. These method steps used by applicant for the adsorbing metal ions and the oxidizing metal ions brings these two types of metal ions sites closely together within molecular nanometer distances, and during a calcining step forms a metal oxide complex having a crystalline structure for providing an effective bi-functional catalyst. Such a close bonding effect for both adsorptive and oxidative metals is not disclosed or suggested by the Zhou patent. Also, for applicants' method, a specific molar ratio range of a binding agent acid such as carboxylic or citric acid to total metals was used. Due to the absence of adsorbing sites on the catalysts as disclosed in this Zhou patent, the NO_x removal efficiency was very low. At 250°C temperature only 70% NO was oxidized, and at 600°C only 75% NO was oxidized, which results are significantly lower than those achieved by applicants' bi-functional catalyst. Accordingly, it is considered that the teachings of Zhou are inconsistent with and do not overcome the deficiency of the primary Tsuchitani et al reference. Thus, due to the deficiencies in the teachings of these cited references regarding applicant's invention as now claimed, it is submitted that new method claims 8-16 are patentable condition and should be allowed.

Previous claim 22, which recited sodium citrate as the carboxylic binding agent, was rejected under 35 U.S.C. 103(a) as being unpatentable over Tsuchitani et al. (U.S. 5,756,057) taken together with Zhou (U.S. 5,759,947), and in further view of Lichtin et al., (U.S. 5,137,703). The Examiner contended that while Tsuchitani et al do not specifically disclose sodium citrate, it would have been obvious to one of ordinary skill to have utilized this known compound, because it is used in the Litchin process (see col. 14, ln 7-8) to make similar catalysts as those of Tsuchitani et al. This sodium citrate is functionally equivalent to the citric acid of Zhou, thus selection of a known equivalence is an obvious matter of choice within skill in the art. Applicants respectfully disagree with this rejection for the additional reasons provided below. It

is pointed out that because the primary Tsuchitani et al reference does not disclose the concept of chemically bonding the adsorption metal oxides and oxidation metal oxides intimately together so as to form a metal oxide complex, it fails to teach or suggest applicant's claimed invention, and this deficiency is not corrected by the secondary references of Zhou and Lichtin et al. Accordingly, this claim (now Claim 11) is also considered to be patentable and should be allowed.

The other prior art patents made of record and considered pertinent to applicant's disclosure but not relied upon have been reviewed, but are not considered to teach or suggest applicants' invention as now being claimed. Although these patents are generally directed to NO_x removal, they either utilize different metals or NO_x reduction instead of combined adsorption and oxidation techniques as disclosed and claimed by applicants.

In view of the additions made to the specification, the new revised claims, and the pertinent arguments as set forth above, it is submitted that the new claims 1-29 are in proper and allowable condition and should be allowed. A reconsideration and allowance of these claims is respectfully solicited.

Respectfully submitted,

Fred A. Wilson

Fred A. Wilson, Agent
Reg. No. 27,019

Hydrocarbon Technologies, Inc.
1501 New York Avenue
Lawrenceville, NJ 08648
(609) 394-3102

CERTIFICATE OF MAILING

This Amendment under 37 CFR 1.113 for patent application Serial No. 10/038120 is being deposited with the U.S. Postal Service as first class mail with sufficient postage addressed to:

Commissioner of Patents and Trademarks
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Date: April 4, 2002

By: Fred A. Wilson